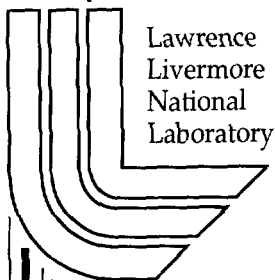


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This article was submitted to
4th International Conference on Modeling and Stimulation of
Microsystems, Hilton Head Island, SC, March 19-21, 2001

U.S. Department of Energy



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December 7, 2000

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This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

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ABSTRACT

Equations for modeling surface chemical kinetics by the interaction of gaseous and surface species are presented. The formulation is embedded in a finite element heat transfer code and an ordinary differential equation package is used to solve the surface system of chemical kinetic equations for each iteration within the heat transfer solver. The method is applied to a flow which includes methane and methanol in a microreactor on a chip. A simpler more conventional method, a plug flow reactor model, is then applied to a similar problem. Initial results for steam reforming of methanol are given.

Keywords: microreactor, heat transfer, surface kinetics

1 INTRODUCTION

Fuel cells and fuel reformers for fuel cells are active areas of inquiry for power applications ranging from about one watt to many megawatts [1]. The complexity of the chemical and thermal phenomena operative in these concepts argue for computationally intense approaches. On the other hand, many concepts are in very early stages of development and rapid scoping calculations are appropriate for screening these concepts and selecting the best for further analysis and /or prototype testing. This work develops and applies computational tools for both the more complex and the simplified approaches. Sample results for microreactors for steam reforming of methanol for fuel cells are contrasted.

2 SURFACE KINETIC MODELING

The surface chemistry formulation begins with the expression for a single chemical reaction:

$$\sum_B \nu_B B = 0 \quad (1)$$

The accepted convention for this form is that the stoichiometric numbers, ν_B , for the products are positive and the reactants are negative. Because surface species do not deplete as a surface reaction progresses (until the full thickness of the substrate is consumed), it is preferable to ignore the sign convention for products and reactants in the

following formulation so that here a less compact form is used:

$$\sum_B \nu_B B - \sum_B \mu_B B = 0 \quad (2)$$

In this form the stoichiometric numbers are all positive and any of the species may appear on both sides of the reaction if desired.

For a set of Q surface reactions between gaseous species and a set of L surface atoms we write:

$$\begin{aligned} \sum_{w=1}^W \nu_{qw} B_w - \sum_{w=1}^W \mu_{qw} B_w \\ + \sum_{l=1}^L \eta_{ql} \theta_l - \sum_{l=1}^L \lambda_{ql} \theta_l = 0 \end{aligned} \quad (3)$$

The gaseous species, B_w , are not variables here, they are constants passed to the surface chemistry formulation from some other processor, for example a CFD solver. The surface atom fractions, θ_l , are the variables. The reaction rates, r_q , for the Q reactions can be written from the above relation:

$$\begin{aligned} r_q = k_{fq} \prod_{w=1}^W [PX_{qw}]^{\nu_{qw}} \prod_{l=1}^L \theta_l^{\eta_{ql}} \\ - k_{rq} \prod_{w=1}^W [PX_{qw}]^{\mu_{qw}} \prod_{l=1}^L \theta_l^{\lambda_{ql}} \end{aligned} \quad (4)$$

where P is pressure and X is mole fraction. The forward and backward reaction rate constants, k_{fq} and k_{rq} , can be specified explicitly or related through the equilibrium constant:

$$K_q = \frac{k_{fq}}{k_{rq}} \quad (5)$$

* Work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

Values for particular equilibrium constants as a function of temperature are given in the JANAF tables [2] or in other chemical references. The following form for the forward reaction rate encompasses a number of prevalent forms [3].

$$k_{fq} = \varepsilon_q f_q S_q e^{T_{aq}/T}$$

$$S_q = 1, \text{ or } S_q = BkT/h \quad (6)$$

$$f_q = P_o / \sqrt{2\pi m_i kT}, \text{ or } f_q = 1$$

The form of f_q follows from the rate at which a gas at pressure P_o bombards a solid surface, rate = $P_o/(2\pi mkT)^{1/2}$, though here P_o is a reference pressure. The value of m above is the mass of the appropriate atom or molecule. The constant T_{aq} is the activation temperature for the onset of the reaction. The S_q term allows for a surface site density, B , to affect the reaction rate.

In this formulation there are L unknown surface concentrations and $4Q$ more unknowns, r_q , k_{rq} , k_{fq} and K_q . The definition of the equilibrium constant, the reaction rate equations and the relations for the reaction rate constants provide $3Q$ relations (when only forward or backward reaction rates are specified). Equilibrium constant data can provide Q more relations.

Finally, the K_q are not independent, since the gaseous mole fractions are interrelated. Thus we can also write:

$$K_q = \prod_{w=1}^W K_w^{y_{q,w}} \prod_{l=1}^L K_l^{u_{q,l}} \quad (7)$$

Here the K_w represent gaseous data and the K_l represent data supplied by any other defined format. The exponential powers, y and u above are determined by the gaseous and the surface chemistry models.

To close the problem L more relations are required. Because the sum of all surface concentrations is unity the derivative of the sum must be zero:

$$\sum_{l=1}^L \frac{\partial \theta_l}{\partial t} = 0 \quad (8)$$

It will be common to treat systems where all but one of the surface atoms are adatoms so that the last surface atom defined is the bare substrate material. In this case it is convenient to rewrite the above relation:

$$\frac{\partial \theta_L}{\partial t} = - \sum_{l=1}^{L-1} \frac{\partial \theta_l}{\partial t} \quad (9)$$

Finally $L-1$ additional relations can be written for the adatoms:

$$\frac{\partial \theta_l}{\partial t} = \sum_{q=1}^Q -\eta_{ql} r_q + \lambda_{ql} r_q \quad (10)$$

These relations express the fact that the rate at which the l -th adatom builds up on the surface is given by the rate that it forms in specific reactions in the set of Q reactions less the rate at which it is desorbed in the Q reactions. For each time step the system of kinetics equations is given the candidate wall temperature and an ordinary differential equation solver (VODE [4]) is used to obtain the surface species concentrations and the reaction rates.

These chemical constraints are coupled to the finite element heat transfer code, TOPAZ3D [5] by a nonlinear heat flux boundary condition. At each time step the conduction equation is solved until the temperature dependent heat load converges. The nodal temperatures and surface shape functions are used to determine a segment wall temperature for the surface kinetics calculation. The surface chemical heat flux is then distributed among the nodes using the segment shape functions.

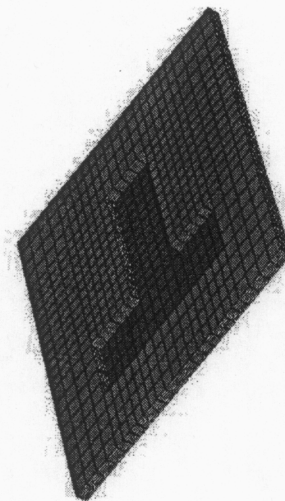
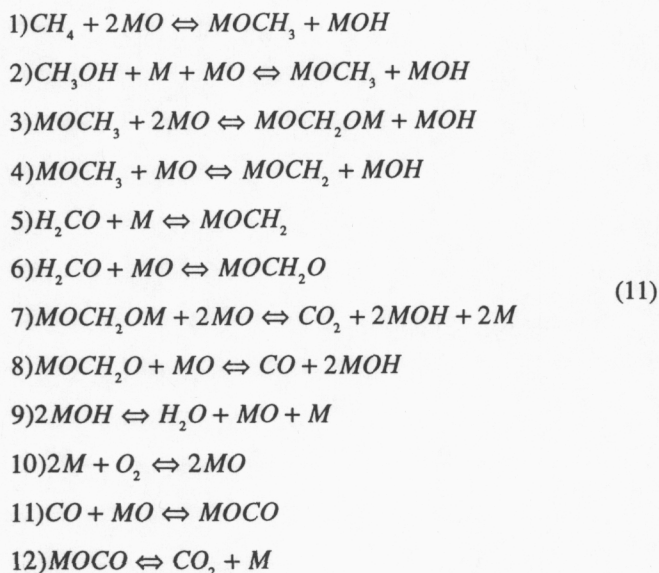


Figure 1. Finite element mesh of silicon wafer with etched microchannel and catalytic surface.

3 SIMPLE MICROREACTOR

The surface chemical kinetic approach was recently applied to the interaction of air and carbon during atmospheric reentry, where heat and mass transfer are strongly dependent on surface mechanisms [3, 6]. It appears likely that enough data also exists for a surface kinetic treatment of steam reforming of methanol [7] but efforts to build such a model have not yet been successful. Results

from the following methane and methanol oxidation system are shown here instead:



The letter M signifies the metal catalyst atom, e.g. molybdenum. Forward and backward rate constants are given in the cited text [7]. This system was exercised for a range of reactant feed compositions and the reaction rates were computed within the finite element conduction solver.

The backing plate to the reactor is not shown. The central channel of the T shaped microreactor is catalyst coated, in this case molybdenum is proposed because that is one catalyst for which the oxidation data is available. The 3. mm by .5 mm channel is etched in silicon. A silicon nitride cover to the silicon wafer is also shown.

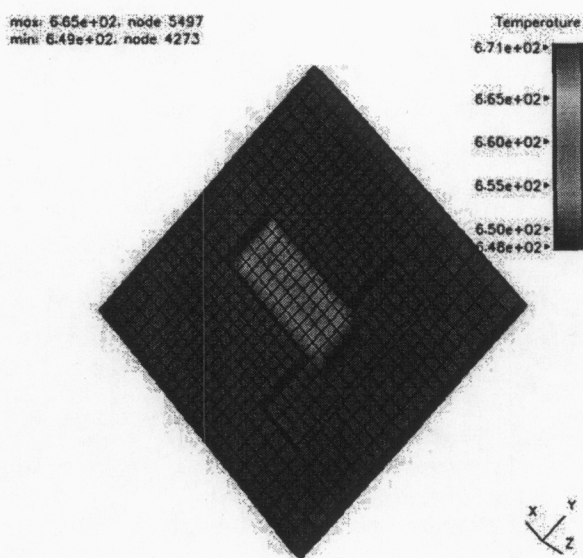


Figure 2. Thermal profile on the catalyst coated portion of the reactor channel.

For the reactor shown the temperature profile is benign, thermal gradients across the catalyst are small.

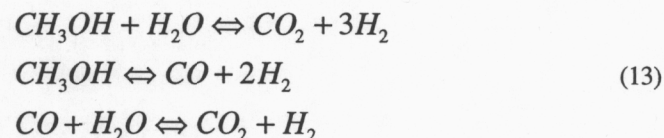
However, hydrogen output would be minimal from a steam reforming reactor. Porous microchannels are a possible alternative.

4 PLUG FLOW REACTOR MODEL

The surface chemical approach is computationally expensive, complex and of limited use for initial scoping of microreactor concepts. A more conventional reactor flow analysis is cheaper, simpler, more useful for screening concepts and able to treat porous catalysts. To this end a plug flow reactor model (PFR) has also been integrated into TOPAZ3D [5]. Along the same central flow passage of the mesh shown above we apply the PFR differential equation:

$$dF_i = r_i w dx \tag{12}$$

where F_i is the molar flow rate, r_i is the reaction rate and w is the catalyst linear density in kg/m. A PFR model of steam reforming of methanol for fuel cells developed by Amphlett et. al. [1] provides a useful scoping tool. The three overall reactions are:



The rate equations are:

$$\begin{aligned}
 r_{\text{CH}_3\text{OH}} & = -k_1 C_{\text{CH}_3\text{OH}} - k_2 \\
 r_{\text{H}_2\text{O}} & = -k_1 C_{\text{CH}_3\text{OH}} \\
 r_{\text{CO}_2} & = k_1 C_{\text{CH}_3\text{OH}} \\
 r_{\text{CO}} & = k_2 \\
 r_{\text{H}_2} & = 3k_1 C_{\text{CH}_3\text{OH}} + 2k_2
 \end{aligned} \tag{14}$$

The rate constants are

$$\begin{aligned}
 k_1 & = \frac{[A_1 + B_1 \ln\{S/M\}] \exp\{-E_1 / R_u T\}}{P^{D_1}} \\
 k_2 & = \frac{A_2 \exp\{-E_2 / R_u T\}}{P^{D_2}}
 \end{aligned} \tag{15}$$

Constants in the above equations were obtained through extensive testing and are given in the reference [1]. Feed rates to the reactor are given as inputs, usually with a steam to methanol ratio (S/M) of 1.1 and conversion efficiencies on the order of 0.5 to 0.9 are computed for the channel geometry shown assuming a reasonable packing fraction for the catalyst.

Solution of the PFR system defines entrance and exit enthalpies for the flow region above each axial position in

the flow channel. A steady flow heat balance on a control volume (CV) one finite element long in the channel gives

$$\sum_i F_i h_{in_i} = \sum_i F_i h_{out_i} + Q_{rxn} - Q_{convn} \quad (16)$$

The summation terms give the enthalpy flows. The heat produced or removed by the progress of the chemical reaction in the system is provided by the solution to the PFR equations. The convection transport term defines the coupling between the fluid flow system and the solid conduction system. For scoping studies it is adequate to set two modes of coupling, either the flow is given an inlet temperature which holds for the whole flow passage (an ideal isothermal reactor which assumes the mesh thermal configuration is perfectly tailored to the flow) or the flow is given the average local temperature of the surrounding mesh (a non-ideal reactor often with poor conversion efficiency). The first option is useful for finding preferred operating conditions while the second is useful for iterating to a configuration which is practical. A fully consistent coupling option is also in work.

For an inlet flow of 1.08×10^{-6} gm-mol/sec of CH_3OH , the first option gives a conversion efficiency of .98 for a packing density of 2.55×10^{-3} kg/m. Outlet flow includes 0.31×10^{-5} gm-mol/sec of H_2 .

The second fluid to solid coupling option was used in a sequence of calculations to compute more realistic performance. For the same inlet flows a conversion efficiency of .64 was obtained. Comparison of figures 3 and 4 indicates that further iterations with the thermal configuration are needed to elevate the hydrogen output: the molar flow rate of H_2 is still rising in figure 4.

Optimizing the thermal profile, enhancing hydrogen output and a fully consistent solid to fluid coupling are priorities for future work.

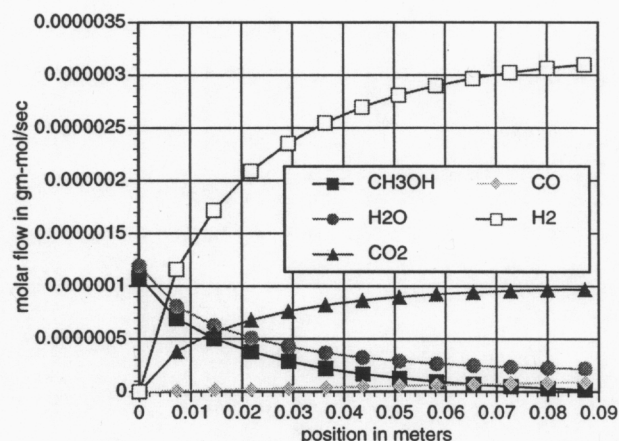


Figure 3. Molar flow rates versus axial position for porous microchannel (inlet fluid temperature imposed for entire channel length).

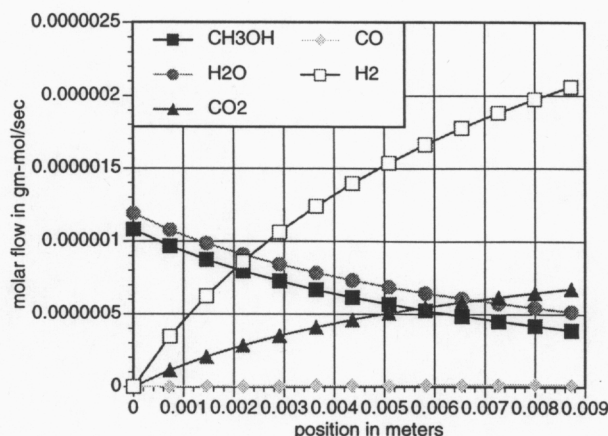


Figure 4. Molar flow rates versus axial position for porous microchannel (fluid temperature reaches surroundings temperature at each axial position).

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